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CATALYSIS IN INDUSTRY



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The review deals with ionic liquid based catalytic systems for intensification of the reaction of olefin oxides with carbon dioxide. Ionic liquids based on derivatives of imidazole, pyridine, tertiary ammonia salts etc. are shown to be highly active to the processes under consideration; they can be used, under certain conditions, as alternatives to the traditional catalysts for cyclocarboxylation of olefin oxides. Specifics of the interaction between oxiranes and carbon dioxide in the presence on ionic liquids including the ones with promoting agents based on metal salts are considered. The mechanisms of the catalytic action of ionic liquids during synthesis of cyclocarbonates are discussed. Publications in the new field of catalytic cyclocarboxylation of olefin oxides in the presence of ionic liquids are inspected.

Keywords: cyclic carbonates, olefin oxides, carbon dioxide, carboxylation, ionic liquids, catalysis.

Methanol Dehydrogenation over Cu-containing Catalysts 17

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Comparative studies of Cu-containing oxide catalysts with different chemical and phase compositions and thermodynamic analysis were aimed at identifying conditions for highly selective process of vapor-phase dehydrogenation of methanol to methyl formate or synthesis gas. It was shown that Cu⁰ nanoparticles formed during the reductive activation are differently selective to the formation of methyl formate from methanol and to its dehydrogenation to form synthesis gas. The proper choice of the catalyst composition and process conditions may provide a high selectivity (90–100 %) either to methyl formate or to synthesis gas. The catalysts based on the zincsilite type Cu-Zn hydroxosilicate and on CuAlZn aurichalcite are highly selective to methyl formate. The experimental data obtained with the most effective catalyst Cu/SiO₂ for dehydrogenation to synthesis gas demonstrate that the yield of synthesis gas can reach 20 m³/h at the 1 atm pressure of methanol vapor, 200 °C and 0,5 s contact time.

Keywords: dehydrogenation of methanol, methyl formate, synthesis gas, partial equilibrium.

New Method for Production of Substituted Anthraquinones via Diene Synthesis in the Presence of Mo-V-P Heteropoly Acid Solution: Catalyst Regeneration 24

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Feasibility of catalytic synthesis of 2-methylanthraquinone from 1,4-naphthaquinone (NQ) and isoprene and of synthesis of 2,3-dimethylanthraquinone from NQ and 2,3-dimethylbutadiene in the presence of an aqueous solution of high-vanadium heteropoly acid (HPA) as the bi-functional catalyst was demonstrated. Two methods for the catalyst regeneration are discussed: oxidation with oxygen at $P_{O_2} = 0,3+0,4$ MPa and with nitric acid at atmospheric pressure. It is shown that the regeneration with nitric acid provides deeper oxidation of the reduced catalyst. The full catalyst recovery after the regeneration allows its recycling in the processes under discussion.

Keywords: substituted anthraquinones, heteropoly acid, regeneration.

CATALYSIS IN PETROLEUM REFINING INDUSTRY

Prospects of Mo- and W-containing Catalysts for Hydroisomerization: Patent Survey. 1. Catalysts Based on Molybdenum and Tungsten Carbides 31

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The analysis of the patent information was conducted in the field of methods of preparation and use of catalytic systems containing carbides of molybdenum and tungsten in the processes of hydroisomerization of paraffin hydrocarbons. The analysis of patent information showed that the modification of acidic carriers by carbides of molybdenum and tungsten allows solving the problem of creating a stable catalyst for hydroisomerization of paraffin fractions resistant to sulfur contaminants in the raw materials of hydroisomerization.

Keywords: molybdenum, tungsten, carbides, oxycarbides, acidic carrier, catalyst, hydrogenation, isomerization.

CATALYSIS AND ENVIRONMENTAL PROTECTION

Improved Adsorptive-Catalytic Process for VOC Removal from Waste Gases 38

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The paper deals with the development of new methods for arrangement of adsorptive-catalytic processes for removal of volatile organic compounds (VOC) from industrial waste gases. Among the suggested new technologies are, e.g., a system with the localized heating of a part of the catalyst bed to initiate burning of sorbed VOC and a system with the adsorption-catalytic bed separated into parallel sections with their non-simultaneous regeneration. The studies were accomplished by combining pilot-scale experiments and mathematical modeling. The arrangement of the initiating heater inside the adsorbent-catalyst bed is shown to allow the energy consumption for regeneration, including specific energy consumption for cleaning unit volume of waste gases and the required heater capacity, to be reduced considerably (by more than two orders of magnitude). Separation of the bed into sections makes it possible to decrease several times the maximal concentration of impurities and the outlet gas temperature during operation. The suggested highly effective and energy saving technologies can be widely used for the atmosphere protection against VOC pollution.

Keywords: adsorptive-catalytic process, volatile organic compounds, catalyst, mathematical modeling, experimental studies, energy consumption, purification degree.

ENGINEERING PROBLEMS

Modernization of Industrial Technology for Dehydrogenation of Methylbutenes to Isoprene.

Part 2. Analysis of the Results of Pilot Testing and Industrial Implementation of the Improved Process 49

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Pilot testing of the technology for dehydrogenation of methylbutenes to isoprene was achieved using a two-reactor system with additional overheated steam fed to the inter-reactor space. A pilot setup with two adiabatic reactors was used at the total ZhKD-3 catalyst loading 60,0 dm³, 565–620 °C, contact time 0,18–0,25 s, feed to steam mass ratio C₅H₁₀ 1,0 : (6,0+30,0) and extra pressure 0,6–0,8 kg/cm². Dependence of the isoprene concentration in the contact gas on the heat energy supplied by the feed and steam was determined under the traditional process conditions and in the pseudoisothermic mode, the latter was achieved by feeding additional overheated steam to the inter-reactor space. 10–12 % increase in the isoprene yield was demonstrated in the improved process. The industrial process conditions were determined on the basis of the results obtained. The improved process was tested at a Nizhnekamsk plant using a setup for dehydrogenation of methylbutenes in a reactor with the catalyst loaded in two beds with 9 t of the catalyst in each. Regularities established during pilot testing were, in general, proved true, while the selectivity was lower because of some design drawbacks to be eliminated. Reliability of the mathematical model was proved by comparing experimental and calculated data.

Keywords: dehydrogenation of methylbutenes to isoprene, pilot testing, mathematical modeling of the process flowsheet.

BIOCATALYSIS

Prospects of the Application of Enzymatic Oil Re-Esterification for the Production of Modified Fats 57

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The paper is a review of the state-of-the-art in the area of enzymatic biocatalysis for synthesis of modified edible fats. Under discussion are properties of biocatalysts, both under development and industrially used, for enzymatic re-esterification of plant oils. Main R&D fields of new biocatalysts including those based on new recombinant lipases, as well as possibility of intentional variations in the contents of certain oil components through arrangement of the catalytic process, are considered. Relevance of the enzymatic re-esterification of oils for designing energy-efficient and ecologically sound production of high-quality food with the required properties is demonstrated.

Keywords: edible oil, lipase, re-esterification, immobilized enzymes, biocatalysis.

Enzymatic Synthesis of Fusil Oil Butyrates 64

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Numerous esters of lower aliphatic acids with alcohols smell nice; they occur in plants, some of them are produced chemically and used as fragrances. In the present work, fruity flavored butyric esters were synthesized using lipase agents, the substrate was the alcohol-con-

taining fraction obtained by distillation of fusil oil (a waste product of alcohol industry, $t_b = 120\text{--}140$ °C. The yield of the target products was ca. 94,0 % in the presence of pancreatic lipase and lipase from yeast *Candida rugosa* under identified optimal conditions.

Keywords: butyrates, synthesis of aromatic substances, pancreatic lipase, lipase from yeast *Candida rugosa*.

Comparison of Lactic Acid Production by Free and PVA-Cryogel-Immobilized Bacteria or Filamentous Fungi	69
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There are results of investigations and comparative analysis of obtained process characteristics of lactic acid (LA) production from glucose within long-term batch process use of various samples of biocatalysts being bacterial *L. casei* and filamentous fungus *R. oryzae* cells in concentrated (immobilized into poly(vinyl alcohol) cryogel or suspended) form. It was revealed for both bacteria and fungus cells that their use in immobilized into PVA-cryogel form is more reasonable as compared to concentrated suspended form since the period of their half-life-time increased in 6 and more times. Actually similar concentrations of LA were produced by immobilized fungus (920 ± 5 g) and bacterial (895 ± 5 g) biocatalysts during their 200 h-batch use, but twice increased level of substrate conversion into LA was obtained for fungus cells (0,92 g LA/g glucose), and the half-life-time of immobilized fungus biocatalyst appeared to be 10 times higher (80 days equal to 96 working cycles) then it was established for immobilized bacterial cells. The comparison between obtained and previously known from literature data showed that application of fungus cells immobilized into PVA-cryogel for LA-production is promising since the results of their usage surpass all processes by main characteristics: level of glucose conversion to LA and maximal accumulated product concentration.

Keywords: lactic acid, immobilized cells, biocatalysts, *Lactobacillus casei*, *Rhizopus oryzae*, poly(vinyl alcohol) cryogel.

Mechanically Activated Enzymatic Hydrolysis of Yeast Biomass.....	76
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Experimental studies were focused on the processes that occur during mechanoenzymatic hydrolysis of cell wall polymers of yeast *Saccharomyces cerevisiae*. Particular attention was paid to the reactivities of polymers involved in the supramolecular structures of the cell walls, as well as to the technology scaling-up using pilot and industrial facilities. The Russian commercially available enzymatic agent CelloLux 2000 (from Sibbiofarm LLC, Berdsk) was used for the studies. It was shown that mechanical treatment of the yeast biomass allows the supramolecular structure of cell wall polymers to be changed and their reactivity to enzymatic hydrolysis to be improved. The yields of mannanoligosaccharide (1,1 %) and mannanoproteins (2,7 %) to the alkali extract were determined. A phenomenological model based on autolocalized process mechanism was suggested for the mechanically activated enzymatic hydrolysis. Pilot and industrial facilities of Sibbiofarm LLC was used for the technology scaling-up and for preparation of the new mannanoligosaccharide product for animal industry. A pilot batch of the product was tested, its efficiency in fighting salmonellosis and gaining in weight of animals demonstrated.

Keywords: mechanical pretreatment, enzymatic hydrolysis, yeast biomass, mannanoligosaccharide, supramolecular structure, scaling-up.

CHRONICLE

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